



United States Environmental Protection Agency
Office of Enforcement and Compliance Assurance
Office of Criminal Enforcement, Forensics and Training

National Enforcement Investigations Center

NEIC

**NEICVP1456E04
Replacement Report**

**NEIC CIVIL INVESTIGATION REPORT
GMAP Region 6 Pollution Accountability Team FY2022**

Calcasieu Parish, Louisiana
St. Charles Parish, Louisiana
St. James Parish, Louisiana
St. John the Baptist Parish, Louisiana

Investigation Dates:
April 11-23, 2022

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and provides a clear indication of the end of this report.**

INVESTIGATION OVERVIEW

This report (NEICVP1456E04) replaces the following U.S. Environmental Protection Agency (EPA) National Enforcement Investigations Center (NEIC) report in its entirety: NEICVP1456E02 (July 2022). This replacement was necessary to correct the following: the reference to the NEIC report NEICVP1456E01 has been updated to reference the NEIC replacement report NEICVP1456E03.

This report supplements U.S. Environmental Protection Agency (EPA) National Enforcement Investigations Center (NEIC) report NEICVP1456E03 with additional data provided by the Picarro G2920 cavity ring-down spectrometer (CRDS) instrument, which measured ethylene oxide (EtO) and methane (CH₄) concentrations, and maps developed from these measurements. The CRDS was installed in NEIC's Geospatial Measurement of Air Pollution (GMAP) vehicle for this investigation. These measurements were not provided in report NEICVP1456E03 because results of laboratory analysis performed by Eastern Research Group (ERG) of canisters collected during the GMAP survey were not yet available at the time of the preparation of the original report. These analytical results were necessary to confirm EtO responses as measured by the CRDS. This report also describes additional steps taken to validate these results. Report NEICVP1456E03 provides detailed information on the events of the survey, which are not repeated in this report. Field measurements from the CRDS were processed into files in Keyhole Markup Language (KML) format and are provided in **Appendix A**.

METHODOLOGY

INSTRUMENTATION

The Picarro G2920 instrument can measure EtO, CH₄, carbon dioxide, and water vapor. The instrument was integrated into the other on-board GMAP instruments for the purposes of this project by Richard Helmich and Ali Gitipour.

CALIBRATION

Calibration verifications for the CRDS were performed at the beginning and the end of each working day. The gas cylinders used for calibration verification of EtO and CH₄ were maintained in a separate trailer. Corresponding calibration gases were metered from the cylinders through a valved manifold. The calibration gases used for the CRDS were single-component calibration mixtures of EtO and CH₄. Detailed descriptions and certificates of analysis of the calibration gases are in the project file. Calibration verifications also included analysis of a “ultra zero air” that contains, at most, only very small quantities of any analyte.

Time periods during the calibration process when relatively constant zero gas and calibration gas responses were obtained were visually identified by Bradley Venner. A summary of the daily quantitative calibration results is shown in **Table 1**.

Table 1. SUMMARY OF DAILY CALIBRATION VERIFICATION RESULTS						
Calibration Level (Span or Zero)	Analyte	Unit	Calibration Standard Concentration	Average Measured Concentration of Calibration Events	Standard Deviation Between Calibration Events	Pooled Standard Deviation Within Calibration Events
Span	EtO	parts per billion (ppb)	105.4	65.2	0.7	0.4
Span	CH ₄	parts per million (ppm)	20.4	20.3	0.01	0.06
Zero	EtO	ppb	0	-0.1	0.1	0.3
Zero	CH ₄	ppm	0	0.0	0.0	0.0

The average calibration response of EtO was 65.2 ppb, and the stated value of the calibration response was 105.4 ppb, so the average recovery of the calibration standard was 62%. This response was stable; the variation in the average calibration response during the run was 0.7 ppb, a 1% relative standard deviation. This may imply that measurement results could be as much as 162% higher than observed. Given the high precision of the instrument, this should be considered an upper uncertainty bound on the measured results. Plots of the calibration results used to calculate these values are shown in **Appendix B**.

During the calibration process, introducing or turning off the CH₄ gas often resulted in an intermittent EtO response. This response could be positive, negative, or oscillating. The CH₄ concentration in the calibration gas was 20 ppm, and the Picarro G2920 instrument is stated to be compatible with CH₄ concentrations between 0 and 10 ppm, so this response may be an artifact of the scale switching routine in the software. As shown by the calibration results after the instrument completed the electronic scale adjustment, the concentration measured was congruent with the certificated concentration. As discussed below, similar behavior was seen when high CH₄ concentrations were encountered in the field.

DATA MANAGEMENT

Following the completion of field activities, data files were processed by the custom application software Google Earth Map Plotter, version 1.7. This software produces KML files that can be opened using geographic information systems such as Google Earth Pro (GEP).

Fixed mapping scales were used for CH₄ and EtO. The minimum mapping scale (green) was set at 2 ppm and 2 ppb for CH₄ and EtO, respectively. The maximum mapping scale (red) was set at 4 ppm and 5 ppb for CH₄ and EtO, respectively. Values greater than maximum mapping scale appear on the maps as proportionally taller red bars.

QUALITY ASSURANCE

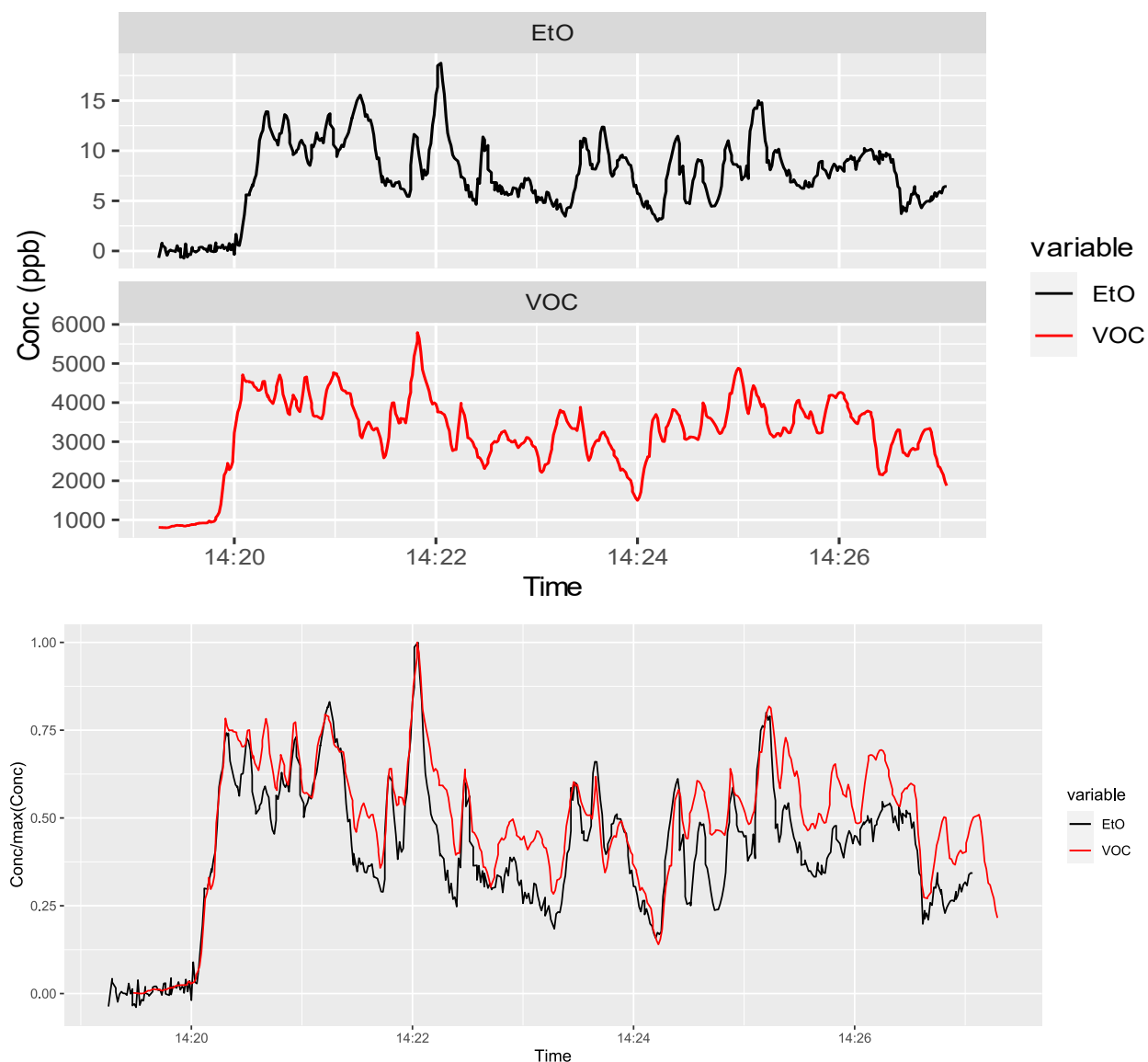
All sampling and measurements, including GMAP measurements and the canister analysis performed by ERG, that are described in this report are not within the scope of NEIC's ISO/IEC 17025 accreditation issued by the ANSI National Accreditation Board (certificate No. FT-0303).

During the data analysis process, a delay was observed in the response of the CRDS when compared to the volatile organic compound (VOC) measurements. This delay could be detected during the collection of some VOC measurements, where a very similar response could be observed in the EtO measurements. The magnitude of the delay was roughly 13 seconds, although there was some day-to-day variation of a second or two. The reason for the delay has not been identified. The delay is unlikely to be due to the photo-ionization detector (PID) instrument since it is located on the main sample trunk and an immediate response of the PID instrument to calibration gases is observed.

An example of the delay is shown in **Figure 1**. This figure shows the measured EtO concentrations by the CRDS and the measured VOC concentrations by the PID. It also shows both responses on the same graph, normalized to their maximum values, but with the VOC

response delayed by 12.5 seconds.¹ The maximum concentration for VOCs on this mapping run was 5,793 ppb, and the maximum concentration for EtO was 18.7 ppb. The qualitative resemblance between the two responses is visually apparent, with multiple peaks matching exactly and parallel behavior on several other peaks.

Figure 1. EtO and VOC response, with overlay of VOC response on EtO response delayed by 12.5 seconds.
Mapping ID: 220413_MA26



The delay introduces some uncertainty as to the wind conditions that prevailed at the time of a recorded CRDS reading. This report presents maps that correlate the wind speed and direction recorded at time t , with the CRDS reading recorded at time $t + d$, where d is the duration of the delay. To create these maps, modified data files were prepared by projecting the CRDS readings and a row identifier into a separate data table, subtracting 13 from the row identifier, and then

¹ VOC data for the GMAP survey are available in report NEICVP1456E03.

merging the separate data table into the original file using the row identifier. Since instrumental responses are recorded roughly every second, this approach corresponds to a 13-second delay but avoids the complexity of the approximate merge that would be required by using the recorded time value. Although this procedure means that the exact value of the delay can vary from map to map, this variation should be less than 1 second. Maps prepared using this method should be interpreted with some caution, particularly when wind directions are highly variable, and the exact value of the delay can impact the attributed wind speed and direction.

Another data quality concern is the potential that the observed EtO response was not specific to EtO but could be the result of an interferent. This survey involved some near-field measurements of relatively high VOC concentrations (e.g., at the parts per million level) while measuring EtO at low concentrations (e.g., at the parts per billion level). An example of this type of situation is illustrated in Figure 1, where the observed VOC concentrations were much higher than the observed EtO concentrations. Although the observed correlation does not prove that there was an interference, this potential must be recognized.

An important measure of the specificity of the CRDS measurement can be obtained by comparing the EtO concentration measured in the canister to the average EtO concentration measured by the CRDS during the canister sampling time. The average EtO concentration was calculated both with and without the delay. The results of this comparison are shown in **Table 2**.

Table 2. COMPARISON OF ETO RESULTS FROM CRDS AND CANISTER ANALYSIS				
Canister_ID	Map_ID	EtO, ppb (CRDS, no delay)	EtO, ppb (CRDS, with delay)	EtO, ppb (Canister)
3071	220411_MA10	<2	<2	0.09
10027	220411_MA14	<2	<2	0.08
3101	220411_MA28	<2	<2	0.04
3068	220411_MA35	<2	<2	0.04
4612	220412_MA01	<2	<2	0.15
521	220412_MA24	<2	<2	0.05
3116	220412_MA41	<2	<2	0.04
9497	220412_MA47	<2	<2	0.11
4621	220413_MA12	<2	<2	0.57
4609	220413_MA16	3.6	3.3	5.39
4605	220414_MA36	<2	<2	0.07
10007	220414_MA42	<2	<2	0.06
10009	220415_MA03	<2	<2	0.07
9490	220415_MA07	<2	<2	0.06
3066	220416_MA24	5.5	5.3	5.13
4606	220418_MA13	3.3	<2	1.59
527	220418_MA54	<2	<2	0.06

Table 2. COMPARISON OF ETO RESULTS FROM CRDS AND CANISTER ANALYSIS				
Canister_ID	Map_ID	EtO, ppb (CRDS, no delay)	EtO, ppb (CRDS, with delay)	EtO, ppb (Canister)
535	220418_MA56	<2	<2	0.06
278	220419_MA17	12.5	13.1	19
10018	220419_MA23	5.9	5.2	10.4
118	220419_MA35	7	6.4	8.62
4602	220420_MA08	<2	<2	0.22
3073	220421_MA32	<2	<2	0.14
4618	220421_MA37	<2	<2	0.33
279	220421_MA39	<2	<2	ND
4601	220421_MA54	<2	<2	0.25
10008	220422_MA11	<2	<2	0.08
519	220422_MA18	<2	<2	ND

The EtO response also depends upon the CH₄ response of the instrument. The Picarro G2920 instrument is only stated to be consistent with CH₄ concentrations between 0 and 10 ppm. On several occasions during field measurements, CH₄ concentrations higher than 10 ppm were observed, and these resulted in an EtO response, which could be positive, negative, or oscillating. A similar phenomenon was observed during instrument calibration, when negative EtO values were sometimes observed at the same time as a change in the CH₄ calibration gas flow (on or off).

Therefore, a quality assurance screen was conducted on each mapping ID for which the average EtO response was greater than 3 ppb. Maps were excluded from this report when CH₄ concentrations were outside the recommended range or had strong correlations with VOCs and for which there were no known EtO sources.

KML files were included for each mapping run that passed the quality assurance screening process. The resulting KML files are provided electronically as **Appendix A**. The results of the quality screen are provided in **Appendix C**.

The GMAP AirMar instrument (wind speed and direction sensor) failed to provide wind speed and direction data on several occasions. The most severe outages occurred on April 11, 2022, and April 22, 2022, when approximately 50% and 0%, respectively, of the wind speed and direction data were recorded. However, most survey days had at least one partial outage. During malfunction events, source attribution can be more challenging. Wind speed and direction data from the National Weather Service at nearby locations can be examined in the absence of data from the AirMar.²

² <https://www.weather.gov/help-past-weather>, accessed May 16, 2022.

RESULTS

GMAP field measurement activities were conducted on 12 days during the investigation period. Detailed information of GMAP activities, indexed by mapping run, are provided in report NEICVP1456E03.

DISCUSSION

GMAP data are best used to screen for areas where further investigation using more traditional inspection and leak detection instruments can help to determine if emissions meet regulatory requirements.

Wind direction provides an important, but not infallible, source of information on the direction of potential emissions sources. For example, when the wind direction is changing frequently, a measured concentration may also be from an emitted plume that has been blown back to the source. Large obstructions such as tanks also have wakes that can generate local winds opposite of the prevailing wind direction. Additionally, the AirMar is located on top of the moving vehicle and can be affected by the vehicle slipstream at higher speeds. To avoid issues with vehicle slipstream causing erroneous wind data, the data is only recorded when the vehicle's speed is less than 25 miles per hour. The wind direction is determined with an internal magnetic compass that also may be affected by local magnetic fields and large, nearby metallic objects.

Appendix A
KML Files

VP1456E04

GMAP Region 6 Pollution Accountability Team FY2022

Calcasieu Parish, Louisiana

St. Charles Parish, Louisiana

St. James Parish, Louisiana

St. John the Baptist Parish, Louisiana

Please see folder sent with project report for digital KML files.
(51 files)

Appendix B
Graphs of Calibration Results

VP1456E04

GMAP R6 Pollution Accountability Team FY2022

Calcasieu Parish, Louisiana

St. Charles Parish, Louisiana

St. James Parish, Louisiana

St. John the Baptist Parish, Louisiana

4 pages

Figure 1: Ultra-zero gas data and mapping scales, EtO

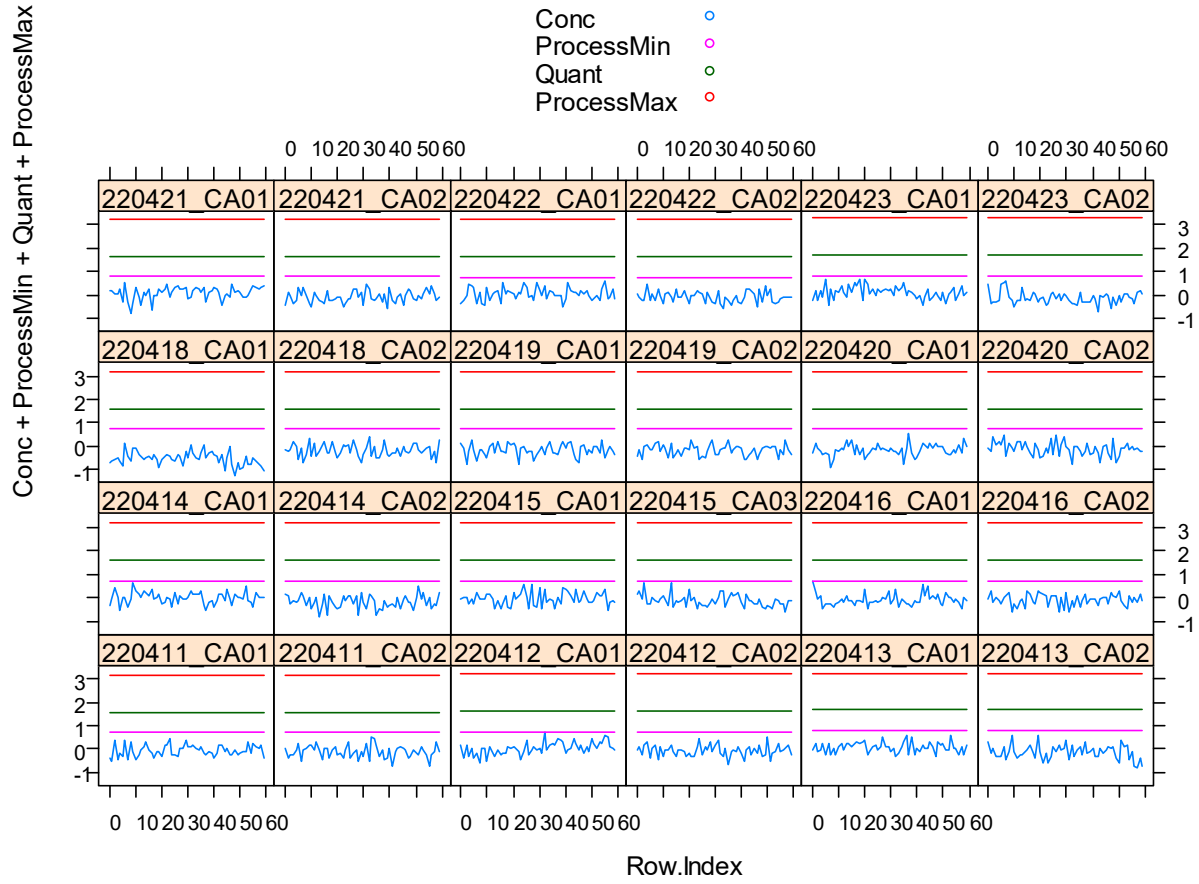


Figure 3: Calibration gas data and mapping scales, EtO

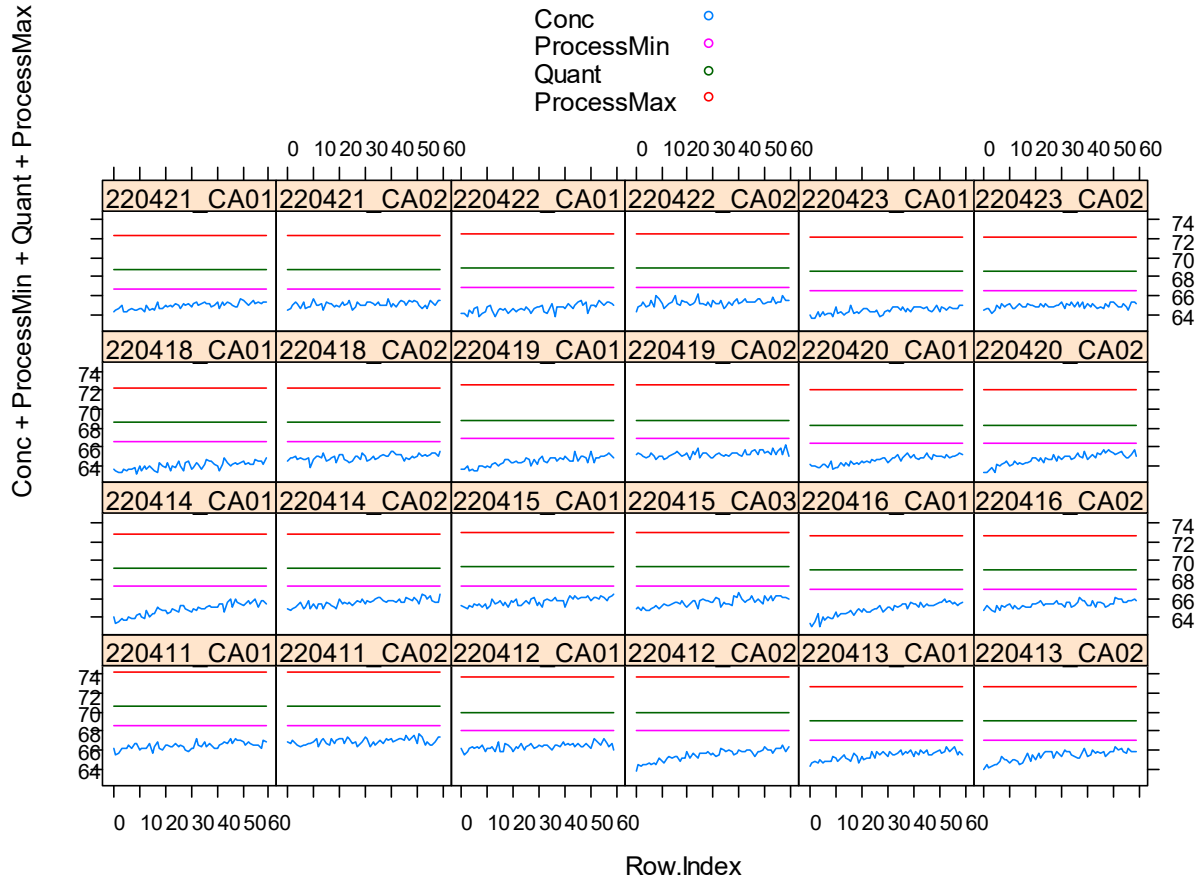
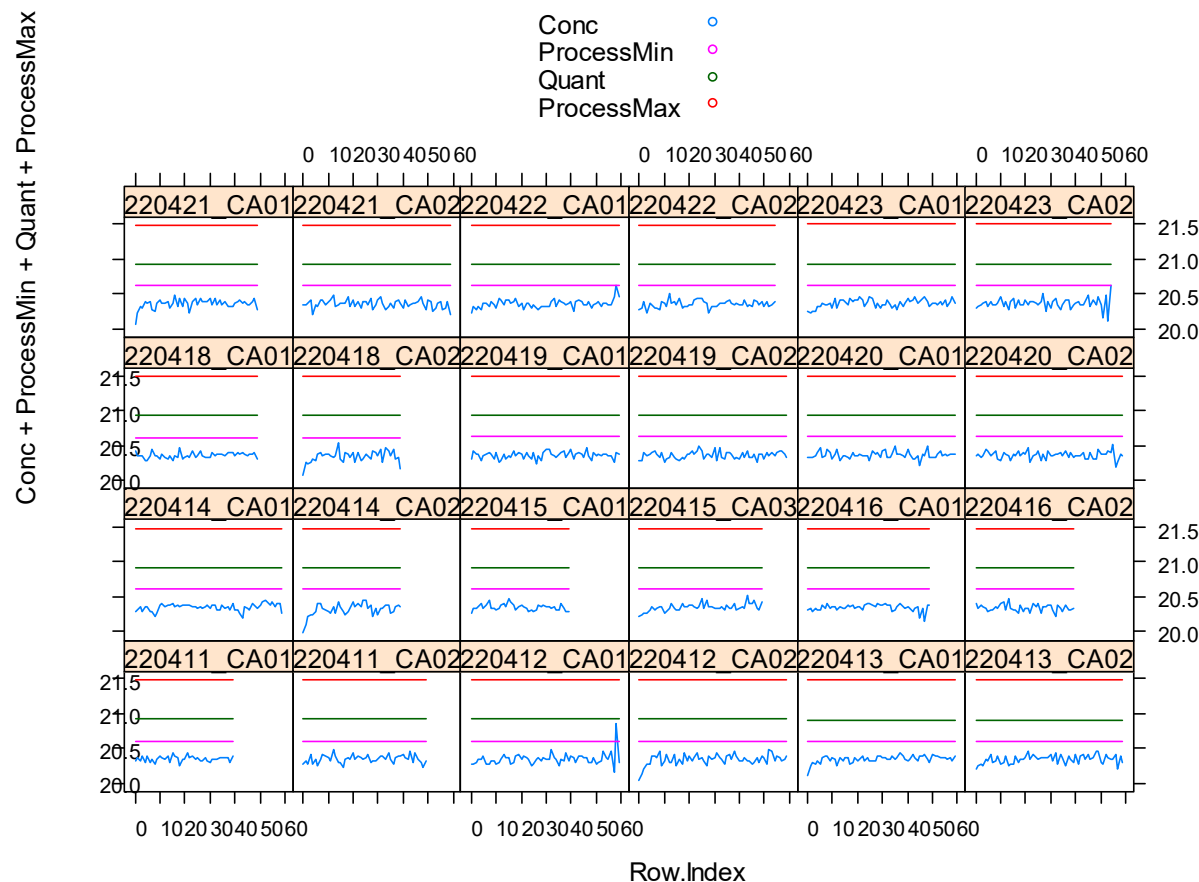


Figure 4: Calibration gas data and mapping scales, CH₄



Appendix C
EtO Quality Assurance Screening Results

VP1456E04
GMAP Region 6 Pollution Accountability Team FY2022
Calcasieu Parish, Louisiana
St. Charles Parish, Louisiana
St. James Parish, Louisiana
St. John the Baptist Parish, Louisiana

3 pages

Map_ID	EtO (ppb)	CH4 (ppm)	Map	Notes
220411_MA09	8.3	11.5	No	Single large EtO negative spike at -7500 ppb
220411_MA13	3.5	2.7	Yes	No clear relation with VOC or CH4
220411_MA14	5.3	4.1	No	Parallel with VOC
220411_MA15	3.3	2.7	No	Below quant; no clear relation with VOC or CH4
220411_MA24	4.5	5.6	No	CH4 greater than 5 ppm; EtO spikes correspond with CH4 peaks
220411_MA35	14.1	2.1	No	Strong correlation with VOC
220412_MA01	8575.3	2.0	No	Peaked VOC plus CH4 goes to zero
220412_MA02	10.5	2.6	No	Strong correlation with VOC but only a single peak
220412_MA08	3.2	2.0	No	Below quant; no clear relation with VOC or CH4
220413_MA04	5.8	2.1	Yes	No clear relation with VOC or CH4
220413_MA08	3.5	2.0	No	Below quant; no clear relation with VOC or CH4
220413_MA09	4.1	2.0	No	Averaged 1 meter bin below quant; ORD canister; No clear relationship with VOC or CH4
220413_MA13	5.0	1.9	Yes	No clear relation with VOC or CH4
220413_MA16	25.0	2.7	Yes	Confirmed by ERG canister
220413_MA24	3.9	5.5	No	Large negative EtO value
220413_MA26	18.7	2.0	No	Parallel with large VOC value
220413_MA27	15.8	1.9	No	Parallel with large VOC value
220413_MA28	13.5	1.9	No	Parallel with large VOC value
220413_MA29	14.5	1.9	No	Parallel with large VOC value
220413_MA30	12.8	2.0	No	Parallel with large VOC value
220413_MA31	15.5	1.9	No	Parallel with large VOC value
220413_MA37	15.7	2.2	No	Parallel with large VOC value
220413_MA38	12.4	2.1	No	Parallel with large VOC value
220413_MA41	11.1	6.6	No	Methane-related spike
220413_MA42	24843.4		No	Methane-related spike
220413_MA43	824.0	7.9	No	Methane-related spike
220413_MA45	13.3	2.3	Possible	No clear relation with VOC or CH4
220413_MA46	4.7	2.0	No	Parallel with large VOC value
220413_MA47	11.2	8.0	Possible	Early hit on EtO followed by methane-related spike
220413_MA48	65.5	2.3	No	Methane-related spike
220413_MA49	13.3	1.9	No	Parallel with VOC value
220413_MA50	22.4	2.0	No	Parallel with VOC value
220413_MA51	16.8	481.8	No	Methane-related spike
220414_MA06	3.0	440.6	No	Methane-related spike
220415_MA35	4.0	2.0	Possible	Brief peak but unrelated to CH4 or VOC
220416_MA23	3.5	2.3	Possible	Brief peak but unrelated to CH4 or VOC
220416_MA24	10.4	2.0	Yes	Confirmed by ERG canister
220416_MA25	7.2	1.9	Yes	Unrelated to CH4 & VOC, vicinity of previous canister
220416_MA27	7.2	1.9	Possible	Peak occurs near peak VOC value but not exact parallel
220416_MA28	3.2	1.9	Possible	Barely over background but unrelated
220418_MA04	5.0	2.1	Possible	Unrelated to CH4 & VOC
220418_MA05	53.4	2.0	No	Parallel to VOC

Map_ID	EtO (ppb)	CH4 (ppm)	Map	Notes
220418_MA07	11.9	2.1	Possible	Unrelated to CH4 & VOC
220418_MA13	29.1	2.0	No	Parallel to VOC
220418_MA63	3.5	2.1	Possible	Brief peak but unrelated to CH4 or VOC
220418_MA68	30.4	2.2	Possible	Somewhat related to VOC but not exact
220418_MA69	8.6	2.1	Possible	Unrelated to CH4 & VOC
220418_MA70	13.5	2.0	Possible	Continued from previous result, unrelated to CH4 and VOC
220418_MA71	10.4	2.0	Possible	Unrelated to CH4 & VOC
220418_MA72	17.0	2.1	Possible	Somewhat related to VOC but not exact
220418_MA73	10.6	2.1	Possible	Somewhat related to VOC but not exact
220419_MA04	9.8	10.6	No	Large negative EtO value
220419_MA09	10.2	2.0	Possible	Unrelated to CH4 & VOC
220419_MA17	23.3	2.1	Possible	Somewhat related to VOC but not exact
220419_MA18	20.4	2.0	Yes	Unrelated to CH4 & VOC
220419_MA19	20.2	2.0	Yes	Unrelated to CH4 & VOC
220419_MA20	12.5	2.1	Possible	Somewhat related to VOC but not exact
220419_MA22	12.0	2.2	Possible	Somewhat related to CH4 but not exact, unrelated to VOC
220419_MA23	16.1	2.2	Yes	Confirmed by ERG canister
220419_MA24	7.2	2.1	Possible	Unrelated to CH4 & VOC
220419_MA26	11.5	2.0	Possible	Unrelated to CH4 & VOC
220419_MA31	4.7	2.4	Possible	Unrelated to CH4 & VOC
220419_MA33	21.9	2.1	No	Parallel to VOC
220419_MA34	12.1	2.1	Possible	Somewhat related to VOC but not exact
220419_MA35	16.4	2.1	Yes	Confirmed by ERG canister
220419_MA36	15.2	2.1	Possible	Somewhat related to VOC but not exact
220419_MA44	5.0	2.4	Possible	Unrelated to CH4 & VOC
220420_MA03	10.0	4.1	Possible	Somewhat related to VOC but not exact
220420_MA04	5.9	2.5	Possible	Somewhat related to CH4 but not exact, unrelated to VOC
220420_MA10	3.6	2.8	Possible	Somewhat related to CH4 but not exact, unrelated to VOC
220420_MA12	3.2	2.9	Possible	Barely over background but unrelated
220420_MA15	9.9	2.3	Possible	Unrelated to CH4 & VOC
220420_MA16	13.6	2.0	Possible	Parallel with VOC but may be co-generated
220420_MA17	13.4	2.1	Possible	Late rise in value prior to end of mapping run
220420_MA18	66.6	6.0	Possible	Somewhat related to VOC but not exact
220420_MA19	7.4	3.3	Possible	Somewhat related to VOC but not exact
220420_MA20	18.2	5.3	Possible	Closely related to VOC but not exact
220420_MA24	6.6	2.4	Possible	Unrelated to CH4 & VOC
220420_MA26	5.6	2.4	Possible	Unrelated to CH4 & VOC
220420_MA27	4.4	2.3	Possible	Looks like drift
220420_MA28	11.0	2.0	Possible	Unrelated to VOC, related to CH4 but at very low levels of CH4
220420_MA29	7.4	2.0	No	Map duration is too short
220420_MA30	9.6	2.5	Possible	Unrelated to CH4 & VOC

Map_ID	EtO (ppb)	CH4 (ppm)	Map	Notes
220420_MA31	10.1	2.4	Possible	Closely related to CH4 but not exact
220421_MA32	7.6	356.9	No	Sharp spike in CH4
220421_MA42	3169.2	25.2	No	CH4 greater than 25 ppm
220421_MA43	11940.7	596.9	No	CH4 greater than 400 ppm; EtO spikes at the same time
220421_MA44	643.9	531.8	No	CH4 greater than 400 ppm; EtO spikes at the same time
220421_MA45	3442.5	14.0	No	CH4 greater than 10 ppm
220421_MA47	3903.5	661.4	No	CH4 greater than 600 ppm; EtO spikes correspond with CH4 peaks
220422_MA25	136.8	16.5	No	CH4 greater than 15 ppm; EtO spikes correspond with CH4 peaks